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(54) Title: A PROCESS FOR THE BLEACHING OF CHEMICAL PULP

(57) Abstract

The invention relates to a process for the bleaching of chemical pulp, process which comprises one or several oxidation steps and one or several alkali treatment steps and in which the pulp is treated with an enzyme. The essential idea of the invention is that the pulp is treated with an enzyme in two or more different steps of the process, an oxidation and/or alkali treatment being most preferably carried out between the enzyme treatment steps. The oxidizing chemical used is most preferably oxygen, although peroxide and/or chlorine and/or chlorine dioxide can also be used in addition to or instead of it, and in the enzyme treatment steps, which preferably number 2-4, the same enzyme or alternatively two or more different enzymes may be used. By the enzyme treatment according to the invention, the amount of toxic organic compounds inthe bleaching effluent is decreased and at the same time the chemical oxygen consumption of the effluent is decreased.

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A process for the bleaching of chemical pulp

The present invention relates to a process for the bleaching of chemical pulp, process which comprises at least one bleaching step and at least one alkali treatment step and in which the pulp is treated with an enzyme.

Especially the chemical pulp obtained by sulfate cooking is brown in color, which is mainly due to lignin remaining in the pulp. Lignin is removed by bleaching, which is usually a multiple-step process in which the pulp is treated alternately with oxidizing chemicals which decompose lignin and with chemicals which dissolve the substances produced as products of the decomposition. The most commonly used oxidizing chemicals have been chorine-containing substances and oxygen, whereas alkali solutions have been used as chemicals removing the decomposition products.

When reacting, the chlorine-containing bleaching chemicals convert the lignin present in the pulp into organic chlorine compounds, which will pass into the bleaching effluents removed from the pulp. The bleaching effluents constitute an environmental problem owing to the potential toxicity of the organic chlorine compounds passing into the effluents, and also the values of chemical oxygen consumption in the bleaching effluents are detrimentally high.

The bleaching effluents which load the environment the worst are produced in the washing steps following the first chlorination and the first alkali step of the bleaching. Efforts have been made to decrease the load by various methods, for example by replacing the chlorine gas with chlorine dioxide or by using oxygen as the oxidizing chemical in the first step. However, fully satisfactory results have not been achieved by these methods. Efforts to decrease the quantities of chlorophenols

and other toxic chlorine compounds in the effluents have indeed been successful, but the values of chemical oxygen consumption of the effluents have not decreased. Therefore, effective biological purification has been needed to back up the said methods.

In recent investigations it has been observed that by using enzymes as an aid in bleaching it is possible to separate lignin and/or hemicellulose from cellulose and to make the pulp in this manner easier to bleach in the subsequent bleaching steps. According to FI Patent Application 881192, the residual chlorine content of a pulp bleached by using chlorine chemicals can also be decreased by an enzyme treatment. It is proposed that the enzyme treatment should in this case be carried out either before the oxidation and alkali steps of the bleaching or after them.

The object of the present invention is to provide a new method, based on enzyme treatment of pulp, by which pulp can be bleached in such a manner that the need for bleaching chemicals decreases and at the same time the chemical oxygen consumption and toxicity of the bleaching effluent decrease so that the need for water purification will be smaller. It is characteristic of the invention that the pulp is treated with an enzyme in two or more steps of the bleaching process, in such a manner that in each enzyme treatment step the pulp is subjected to a treatment substantially different from that in the directly preceding or subsequent step of the process.

According to the invention it has thus been observed that the action of enzymes is enhanced when they are used in several different steps, preferably between the oxidation and alkali steps belonging to the process. It has been noted that an enzyme treatment carried out at the beginning of the bleaching step enables the amount of chlorine chemicals used to be decreased by approx. 25 %, and thus the repeated enzyme treat-

ments according to the invention will result in considerably higher savings in bleaching chemicals.

The expedient number of enzyme treatment steps in the bleaching process according to the invention is from two to four. One preferred process, which includes three enzyme treatment steps, comprises as the first step an enzyme treatment of the pulp obtained from the cooking and as the following steps an oxidation of the pulp with an oxidizing chemical, a second enzyme treatment, a treatment with an alkali, and a third enzyme treatment, in the said order. After these steps the bleaching of the pulp may further continue in one or several bleaching and/or alkali treatment steps.

In order to minimize the amount of organic chlorine compounds in effluents and in the obtained bleached chemical pulp, it is advantageous to use oxygen and/or hydrogen peroxide and/or chlorine dioxide in the oxidation steps of the process. By this procedure the amount of organic chlorine compounds in the effluents can be decreased by more than 90 % also in the bleaching of softwood pulp, which has not been possible by using the prior-art methods.

According to one preferred embodiment of the invention, at least one enzyme treatment step is followed in the process by a treatment with alkali, in which an oxidizing chemical, such as oxygen or peroxide, is used besides the alkali. It has been observed that such an oxidizing alkali treatment decreases especially effectively the need for chlorine chemicals in bleaching.

In the bleaching process according to the invention, the enzyme treatments break down the hemicellulose and/or lignin present in the pulp and make the pulp more porous, thus increasing the action of the chemicals in subsequent pulp treatment steps. The enzyme treatment may be followed by a washing of the pulp,

removing constituents broken down from the pulp; these constituents can be led to a burning so that they will cause no effluent load but the energy contained in them can be exploited in the energy supply of the mill.

With the exception of the enzyme treatment steps, the pulp bleaching according to the invention can be carried out in the conventional manner so that the oxidation and alkali steps alternate. After the various steps the pulp can be washed in order to remove the bleaching chemicals and the broken-down constituents.

According to the invention, the enzyme treatment is preferably carried out within a temperature range of 10-90 °C, preferably within 40-80 °C, and at a pH of 3.3-11.0, preferably 4.0-10.0. The enzyme used may be hemicellulase, cellulase, pectinase, esterase, ligninase, phenol oxidase, or a mixture of the same. Hemicellulases and laccase, which belongs to phenol oxidases, are particularly preferred.

It is possible to use one and the same enzyme, such as hemicellulase, in the enzyme treatments belonging to the process according to the invention. It is also possible that the process includes at least two separate enzyme treatment steps, in which at least two different enzymes are used. The process may thus begin, for example, with a hemicellulase treatment, which is followed by a laccase treatment after the oxidation step, and by another hemicellulase treatment after the subsequent alkali step. When different enzymes are used, the enzyme treatments can also take place successively in the process.

The invention is described below in greater detail with the help of an embodiment example based on laboratory experiments.

Example

To 300 g of pulp solids obtained from pine sulfate cooking

(solids content of pulp 30 %) was added a diluted enzyme mixture Pulpzyme (Novo, hemicellulase) so as to make the consistency of the pulp 10 % and its xylanase activity 5 U/g of pulp solids. Before this the pH of the pulp had been adjusted by means of acetic acid to a level of 5.5-6.0. The temperature of the enzyme treatment was 55 °C and the treatment time 2 h.

After the enzyme treatment the pulp was washed with water.

Next, the pulp was subjected to an oxidizing bleaching treatment by using a mixture which contained 50 % chlorine dioxide and 50 % chlorine gas. The mixture was proportioned at 2.0 x the kappa number after the pulping. The treatment temperature was 40 °C and the treatment time 45 min and the consistency of the pulp 3.5 %.

Next, the pulp was subjected to an alkali treatment by using a 2-% sodium hydroxide solution the proportion of which was 0.9 x kappa. The consistency of the mixture was 10 %, and the treatment temperature was 60 °C and the treatment time 90 min. After the alkali treatment the pulp was washed with a 20-fold amount of water.

Thereafter the bleaching was continued by repeating the enzyme step by using the same enzyme mixture as in the first step and the oxidation step by using chlorine dioxide and by washing the pulp between the steps as described above. In this case the amount of enzyme in the second enzyme treatment was 2.5 U/g of pulp. The amount of chlorine dioxide in the second oxidizing step was 1.5 % of the amount of the pulp being bleached.

The bleached pulp was analyzed. The results are shown in the following Table 1.

In addition to the experiment (Experiment 2) described above and illustrating the invention, a reference experiment (Experi-

ment 1) was carried out, the results of which are also shown in the following Table 1.

The experiments were carried out as follows:
Experiment 1 (reference experiment): the pulp was not subjected to a second enzyme treatment. In other respects the experiment corresponded to that described above (Experiment 2).

Table 1

	Experiment 1 (reference)	Experiment 2
1st enzyme treatment - enzyme proportion (l/t)	1	1
ClO_2/Cl ratio	50/50	50/50
Kappa	27.7	27.7
pH		
- enzyme step	5.4	5.6
- oxidation step (ClO_2/Cl)	2.1	2.1
- alkali step	11.7	11.6
Consumption of active chlorine (%)	5.54	5.54
Intermediate kappa	5.7	5.7
2nd enzyme treatment (l/t)	-	0.5
pH		
- 2nd enzyme step		5.3
- oxidation step (ClO_2)	2.1	2.1
- SO_2 step beginning/end	4.8/3.7	4.8/3.7
Whiteness (ISO)	60.97	67.54

For an expert in the art it is evident that the various embodiments of the invention are not limited to the examples described above but may vary within the scope of the accompanying patent claims.

Claims

1. A process for the bleaching of chemical pulp, process which comprises at minimum one oxidation step and at minimum one alkali treatment step and in which the pulp is treated with an enzyme, **characterized** in that the pulp is treated with an enzyme in two or more steps of the bleaching process in such a manner that in each enzyme treatment step the pulp receives a treatment substantially different from that in the immediately preceding or subsequent process step.

2. A process according to Claim 1, **characterized** in that the process includes 2-4 separate enzyme treatment steps.

3. A process according to Claim 2, **characterized** in that the process includes three separate enzyme treatment steps.

4. A process according to Claim 3, **characterized** in that the first step of the bleaching process is an enzyme treatment of the pulp and the subsequent steps are an oxidation of the pulp with an oxidizing chemical, a second enzyme treatment, a treatment with an alkali, and a third enzyme treatment, in the said sequence, whereafter the bleaching of the pulp is further continued in one or several oxidation and/or alkali treatment steps.

5. A process according to any of the above claims, **characterized** in that the oxidizing chemical used in one or several process steps is oxygen.

6. A process according to any of the above claims, **characterized** in that at least one enzyme treatment step is followed in the process by an alkali treatment in which an oxidizing chemical, such as oxygen or peroxide, is used in addition to the alkali.

7. A process according to Claims 4-6, characterized in that the first step of the process is an enzyme treatment and the subsequent steps are oxidation with oxygen, a second enzyme treatment, an alkali treatment in which oxygen or peroxide is used in addition to alkali, a third enzyme treatment, oxidation with oxygen or chlorine dioxide, an alkali treatment, and oxidation with oxygen or chlorine dioxide, the steps following one another in the said sequence.

8. A process according to any of the above claims, characterized in that the enzyme used is hemicellulase, cellulase, pectinase, esterase, ligninase, and/or phenol oxidase.

9. A process according to any of the above claims, characterized in that the process includes at minimum two separate enzyme treatment steps, in which at minimum two different enzymes are used.

10. A process according to any of the above claims, characterized in that the process is used for bleaching a pulp obtained from softwood, such as pine sulfate pulp.

INTERNATIONAL SEARCH REPORT

International Application No PCT/FI 91/00033

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: D 21 C 9/10

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	D 21 C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in Fields Searched[8]

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
P,A	EP, A2, 0383999 (ENSO-GUTZEIT OY) 29 August 1990, see the whole document --	
P,A	EP, A2, 0406617 (INTERNATIONAL PAPER COMPANY) 9 January 1991, see the whole document --	

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* Special categories of cited documents: [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
12th April 1991	1991 -05- 02
International Searching Authority	**Signature of Authorized Officer**
SWEDISH PATENT OFFICE	Marianne Bratsberg

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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.PCT/FI 91/00033

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the Swedish Patent Office EDP file on 91-02-28
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0383999	90-08-29	JP-A- 2221482	90-09-04
EP-A2- 0406617	91-01-09	NONE	